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Scope of Research

Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of “dreams” for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of not only fundamental chemistry but also opening the way to more extensive application of main group chemistry.

Selected Publications

Tsurusaki, A.; Sasamori, T.; Wakamiya, A.; Yamaguchi, S.; Nagura, K.; Irle, S.; Tokitoh, N., Synthesis of 1-Phospha-2-boraacenaphthenes: Reductive 1,2-Aryl Migration of 1-Diarylboron-8-dichlorophosphinonaphthalenes, *Angew. Chem. Int. Ed.*, **50**, 10940–10943 (2011).

Sugamata, K.; Sasamori, T.; Tokitoh, N., Fluorination Reaction of a Ditelluride Bearing Bulky Aryl Substituents: Formation of Mixed-Valent $\text{Te}^{\text{IV}}\text{--Te}^{\text{II}}$ Ditelluride Difluoride, *Chem. Asian J.*, **6**, 2301–2303 (2011).

KEYWORDS

Steric Protection
Kinetic Stabilization
Low-coordinated Species
Heteroatom
Transition Metal Complexes

LiBr-Assisted Generation of a Silylenoid from 1,2-Dibromodisilene

Silylenoids (R_2SiMX) are the silicon analogues of carbenoids, where X denotes a leaving group (e.g., halogen or alkoxy) and M is a metal atom. Silylenoids have comparable reactivity to silylenes ($R_2Si:$) and react with both electrophiles and nucleophiles. During the course of our studies on 1,2-diaryl-1,2-dibromodisilene **1**, we found the evidence for the LiBr-assisted generation of silylenoid **2** and/or silylene **3** from **1**. This work provides a unique method to the *in situ* generation of silylenes from disilenes. It is noteworthy that the reaction products (e.g., compounds **4–6**) from this study still contain a Si–Br bond, which can be exploited in subsequent reactions.

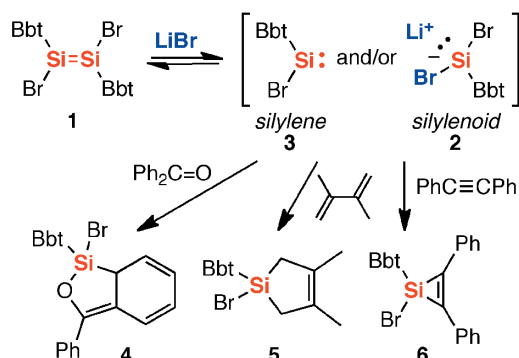
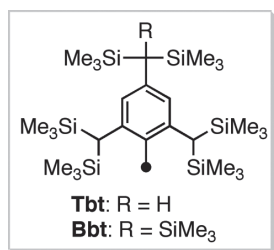


Figure 1. Generation of silylenoid **2**.

1-Phospha-2-boraacenaphthenes

Chemistry of organic π -electron conjugated molecules bearing several main group elements, especially group 13 and/or 15 elements, in their backbones have attracted much attention in recent years from the viewpoint of material science, because group 13 and 15 elements should drastically change the HOMO and LUMO levels of the π -conjugated systems. We have achieved the synthesis of 1,2-diaryl-1-phospha-2-boraacenaphthenes **7**, which are new members of heterocyclic compounds containing a P–B bond. Compounds **7** were synthesized as orange crystals by the reduction of 1-diarylboryl-8-dichlorophosphinonaphthalene via a unique intramolecular migration of the aryl group from the boron to phosphorus atoms. Furthermore, **7** showed orange fluorescence with a large Stokes shift. Both experimental and theoretical results on **7** revealed the significant interaction between a P–B bond and a naphthyl unit.

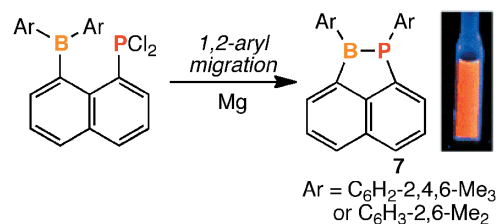


Figure 2. Syntheses of 1-Phospha-2-boraacenaphthenes.

Formation of Te(IV)–Te(II) Mixed-valent Ditelluride Difluoride

Because of their rapid disproportionation reactions, monoorganotellurium(II) monohalides, $R\text{TeX}$, are very unstable and difficult to isolate. Above all, monoorganotellurium(II) monofluorides, $R\text{TeF}$, are extremely unstable compounds, and no organotellurium(II) fluorides kinetically stabilized by bulky organic substituents have been reported, even though there have been a few stable examples of monoorganotellurium(II) halides (Cl, Br, I). We have reported the synthesis and isolation of monoorganotellurium(II) halides kinetically stabilized by a Bbt group. It was found that BbtTeX ($X = \text{Cl}, \text{Br}, \text{I}$) keep their monomeric structures both in solution and in the solid state. In the case of $X = \text{F}$, in contrast, not the expected BbtTeF but a novel species of a Te(IV)–Te(II) mixed-valent ditelluride difluoride, $\text{BbtTe}(\text{F})_2\text{–TeBbt}$ (**9**), was obtained as a stable compound. One of the tellurium atoms exhibits pseudo trigonal bipyramidal geometry as a hypervalent compound, and the two fluorine atoms occupy the apical positions. The NMR study at variable temperature showed its high thermal stability with keeping the mixed-valent structure in solution.

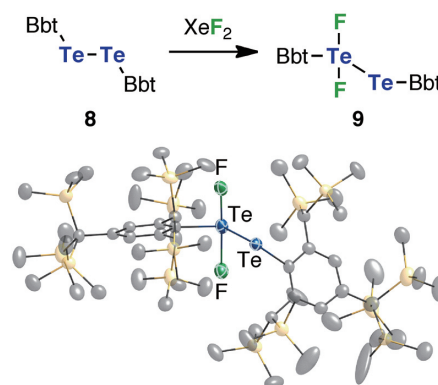


Figure 3. Synthesis and Structure of Mixed-valent Ditelluride Difluoride.